Structural Performance of Nanoquasicrystalline Composites Based on Al-Fe-Cr-alloy:

Synthesis and Key Characteristics

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Abstract — **The present study is primary addressed to structural performance of nanoquasicrystalline composites based on Al-Fe-Cr alloy and, particularly, their thermal stability and mechanical behaviour in response to heat treatment. Several kinds of semi-products and bulk-shaped composites have been produced using rapid solidification by melt spinning, powder atomization, hot extrusion, and cold-spraying. All kinds of as-received products comprised nano-sized quasicrystalline particles embedded in Al matrix although their fraction volume and the other structural parameters of composites were found to be rather different and dependent on synthesized strategy. Evolution of structure in response to heat treatment of the each kind of product and synthesized composite have been studied by means of precise method of differential scanning calorimetry, X-ray analysis, and electron microscopy. Mechanical parameters of as received and heat treated composites have been examined by using indentation technique and discussed by considering classical strengthening mechanisms. As to structural stability of ternary Al-Fe-Cr alloy, cold-spraying technique shows essential advantage in remaining quasicrystalline phase and, hence, mechanical properties compared to that provided by currently employed hot extrusion.**

Keywords — nanoquasicrystals; Al-based composite; thermal stability; microstructure; mechanical properties

I. INTRODUCTION

Quasicrystalline Al–Fe-based alloys are a group of Complex Metallic Alloys (CMAs) designated as a new class of composite material that is characterized by a complex crystallographic structure [1,2]. Formation of quasicrystalline i-phase with long range orientation order and no translational symmetry in rapidly-cooled Al-alloys was originally discovered by Shehtman et al. in 1984 [3] and, then, promoted by additions of Mn, Fe, Cr, V, Ti, Zr, Nb and Ta [4-7]. Quasicrystalline Al-Fe-based CMAs are of growing interest owing to their interesting and sometimes unexpected properties [2,4-6,8]. In particular, nanoquasicrystalline Al–Fe–Cr-based alloys show high elevated-temperature strength ensured by increased structural stability. Moreover, excellent balance between a high strength and sufficient ductility is indicative of quasicrystalline Al–Fe–Cr-based alloys [4-6,9] compared to commercial Al-based alloys recommended for service under elevated temperature. A number of processing routes, which are capable for synthesis of Al-based quasicryctalline alloys owing to required high cooling rate about 10^5 K/s, have been developed last decade. Among the other processes, rapid solidification by melt spinning [7,10] and powder atomisation technique [6,8,11] are thought to be mostly effective for mass production of quasicrystalline semi-products. Presently, hot extrusion and cold spraying technique as alternative process are developed to consolidate quasicrystalline semi-products in bulk shaped composite material [4,6,11-13].

This paper highlights the role of processing route in structural performance of semi-products and bulk-shaped composite material.

II. EXPEROMENTAL

A. Materials and Processing

Quasicrystalline alloy with nominal composition Al94Fe3Cr3 was used in experiments. Quasicrystalline semi-products materials were performed in form of rapidly solidified ribbons produced under reduced argon atmosphere and powder fabricated by water-atomization technique using inhibited high-pressure water with Ph 3.5 [6]. Fraction volume of quasicrystalline particles contained by powder was not higher than 30%. Consolidation of quasicrystalline powder was done in two step process including pre-compaction in hermetic capsule at the temperature of 350 °C during 1 hour which was followed by extrusion at the temperature of 380 °C. In addition, cold-spray technique was used to consolidate quasicrystalline powder in form of thick coatings with thickness about 800 μm. In cold spraying experiments, velocity of air/particle jet was roughly about V=750 m/s while its temperature was as high as 400 °C [13].

B. Structural Characterisation

Structural characterisation was performed by X-ray diffraction (XRD) analysis using Cu Kα radiation. The icosahedral quasicrystalline i-phase was indexed using Cahn's indexation scheme [44]. Scanning and transmission electron microscopy (SEM and TEM) performed by microscopes such as Jeol Superprobe-733 (JEOL, Japan) equipped with X-ray detectors (EDX and EPMA) and JEM 2100 F (JEOL, Japan) were used to obtain basic information concerning microstructural features of materials.

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C. Mechanical Testing

Microhardness measurements were performed using a conventional microhardness machine equipped by standard Vickers' pyramid. Microhardness numbers were determined under indentation loads not higher than 1.0 N. Plasticity characteristic δ_H as dimensionless parameter that may vary in the range from 0 (for "pure" elastic contact) to 1 (for "pure" plastic contact) was derived by calculations through microhardness, HV, and Young's modulus, E [14]. Load-displacement measurements were fulfilled to determine Young's modulus, E, according to the test method procedure proposed by Oliver and Pharr [15].

III. Results and Discussion

A. Structural characterisation of quasicrystalline composites

The results of XRD analysis indicate the presence of icosahedral phase (i-phase) besides α-Al, as can be seen in Fig. 1. However, there are few differences of XRD patterns for as-received bulk materials compared to those for semi-products. In particular, intensity of i-phase reflections presented in XRD pattern for as-extruded samples is much lesser, suggesting reduced fraction volume of quasicrystalline phase. The latter is thought to be partially decomposed during hot extrusion process operated by combined effect of high pressure and enhanced temperature. Actually, weak XRD peak at $2\theta \sim 42.1°$corresponding to the metastable Al_6Fe phase is observed in the XRD pattern of as-extruded material. The above assumption good corresponds to the presence of additional reflections for α-Al, indicating the formation of two α-Al solid solutions with different lattice parameter a_o, and, hence, different elementary composition, see Table I. As opposed to this, cold-spraying offers essential advantages in remaining quasicrystalline particles since adiabatic increase of temperature affects only particle/particle interface while dislocation density of α-Al solid solution increases up to 10^{15} m/m^3.

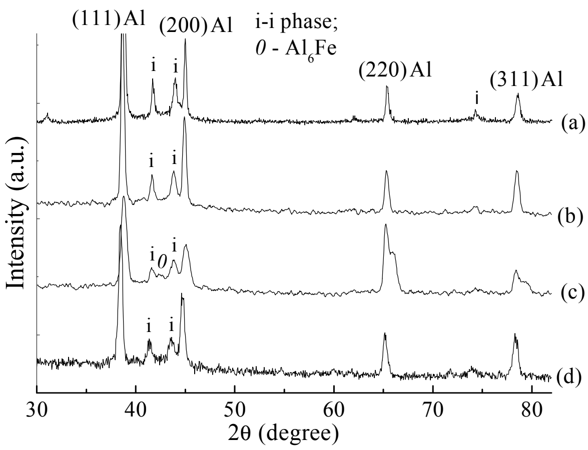

Fig. 1. XRD patterns of (a) as-spun alloy, (b) as-atomized powder, (c) as-extruded material, and (d) as-sprayed alloy

TABLE I. STRUCTURAL PARAMETERS FOR α-Al SOLID SOLUTION

Material	Parameter	
	Lattice parameter, a_o (nm)	*Dislocation density, ρ (m/m^3)*
Melt-spun alloy	0.4037	10^{11}
Atomized powder	0,4042	10^{13}
Extruded material	0.4043 / 0.4011	10^{16}
Cold-sprayed alloy	0.4045	10^{15}

This result is in good agreement with the data published previously [13]. One of the α-Al solid solution has lattice parameter a_o, which is almost the same as that for as-atomized feedstock powder. Another α-Al solid solution demonstrates reduced lattice parameter a_o, suggesting the enrichment of α-Al by dissolved Fe and Cr, which atomic radii are smaller by ~ 12% than the atomic radius of Al. In addition, reflections of α-Al presented in XRD pattern for as-extruded material are found to be broad, suggesting dislocation activity. Actually, dislocation density for α-Al solid solution in extruded material achieves the value $\rho = 10^{16}$ m/m^3 which exceeds by 3 order magnitude compared to that recorded for feedstock atomized powder.

It is noticeable that all reflections corresponding to α-Al solid solution of as-sprayed alloy shift towards smaller 2θ compared to those recorded in the XRD pattern of as-atomized powder. This fact indicates the increase of lattice parameter a_o of α-Al solid solution for as-received cold-sprayed alloy and, thus, its depletion by dissolved Fe and Cr. Actually, lattice parameter a_o of α-Al solid solution for as-sprayed alloy shows the greatest value compared to other products, see Table I.

The results of XRD analysis are in good agreement with the data determined by TEM observation. Fig. 2 displays representative bright field TEM images showing typical morphology of quasicrystalline particles (A) embedded in α-Al matrix. Generally, icosahedral quasicrystalline particles demonstrate rounded and/or rosette-like shape and have the size ranged from 50 to 300 nm. As it is shown in Fig. 2 (a), distinctive feature of microstructure for the as-spun alloy is the presence of grain boundary precipitates (B) and very small particles placed inside the α-Al grains (C), which were identified as those corresponded to metastable crystalline phases, i.e. distorted multiphase θ -$Al_{13}(Fe,Cr)_{2\text{-}4}$ and/or Al_6Fe [7,10].

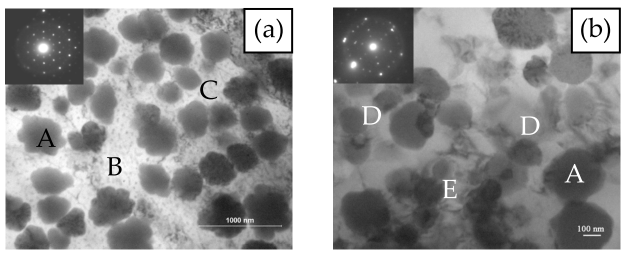

Fig. 2. Bright-field TEM images showing the microstructure of (a) as-spun alloy and (b) as-extruded material: A –quasicrystalline particles, B - grain boundary precipitates; C- fine crystalline particles inside the α-Al grains; D - crystalline particles of rectangular shape; E –dislocation tangle. In (a, b) - SAED patterns corresponded to a single quasicrystalline particle

A few crystals (D) with rectangular shape presumably corresponded to Al_6Fe phase, and dislocation tangles (E) are also visible in microstructure of as-extruded material, see Fig. 2 (b). As-opposed to as-extruded material, no crystalline particles of rectangular shape are found in microstructure of as-sprayed alloy which, however, demonstrates bigger in size quasicrystalline particles and reduced fraction volume of dislocation tangles.

B. Structural stability of quasicrystalline Al-Fe-Cr- alloy

Two exothermic peaks are clearly recognized in DSC runs of all kinds of the samples, see Fig.3. The main exothermic peak B is commonly associated with the process, which involves gradual dissolution of quasicrystalline particles together with simultaneous formation of more stable crystalline Al_6Fe particles and stable intermetallic compounds such as θ-$Al_{13}Fe_4$ and θ-$Al_{13}Cr_2$ [5,7,10,16]. The distinctive feature of DSC run for melt-spun-alloy is additional exothermic peak C overlapping with exothermic peak B. The results of XRD analysis and TEM observation specified that transformation of metastable precipitates into more stable Al_6Fe particles and $Al_{13}(Fe,Cr)_{2\text{-}4}$ multiphases is the reason of exothermic reaction C.

The nature of broad exothermic peak A is rather different since it arises from dislocation reorganization and recrystallization processes within the Al matrix [17]. In the melt-spun alloy, atomized powder, and cold-sprayed alloy, heat flow for exothermic reaction A increases as dislocation density in α-Al matrix increases. It is noticeable that exothermic peak A in DSC run of extruded sample with the highest value of dislocation density within α-Al matrix is omitted. This becomes understanding by considering the fact that recrystallization process would be realized during long-term pre-treatment at the 350 °C. Attention should be paid to important role of dislocation activity in structural stability of bulk-shaped material. In particular, the main exothermic peak B both for extruded material and for cold-sprayed alloy shift by about 50 °C toward lower temperatures, indicating an increased kinetic of quasicrystalline particles decomposition. Of importance is the fact that consolidation of feedstock powder in bulk-shaped material results in a reduction of the main exothermic peak B.

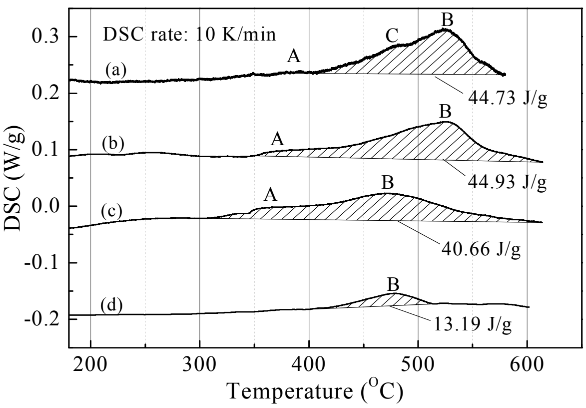

Fig. 3. DSC runs for (a) melt-spun alloy, (b) atomized powder as well as for (c) cold-sprayed alloy and (d) extruded material

However, the decrease of heat flow owing reaction B for cold-spraying is insignificant whereas that for extruded material is great. Adiabatic regime indicative of cold-spraying process leads to considerable overheating particle boundary and, hence, feasible dissolution of some quasicrystals located at the particle/particle interface while the other quasicrystals inside powder particles remain intact. As-opposed to this long-term pre-treatment followed by hot extrusion favors intensified decomposition of quasicrystalline particles.

C. Mechanical response of Al-Fe-Cr-based alloy

Fig. 4 shows microhardness, HV, and plasticity characteristic $\delta_{H,}$ both plotted against heat treatment temperature, T, used in experiments with different kinds of quasicrystalline materials. Several structural regions could be marked out in the above curves. In the initial regions I and II, microhardness, HV, for the melt-spun alloy and cold-sprayed coating decrease slightly whereas those for extruded material keep almost stable values. In the region III, the increase of heat treatment temperature causes the values of microhardness, HV, to reduce down stronger. In the last regions IV and V, the values of the above mechanical parameters decrease dramatically as heat treatment temperature tends to increase up to 600 °C. Of importance is the fact that microhardness, HV, numbers of cold-sprayed coating superior to those of melt-spun alloy and extruded material over the all range of temperatures. Strength properties for different kinds of quasicrystalline alloy are mainly controlled by strengthening mechanisms. In particular, microhardness takes the values as high as possible when quasicrystalline particles are presented in α-Al matrix. Dissolution of quasicrystalls together with simultaneous formation of metastable Al_6Fe particles and, especially, particles of stable θ-phases causes microhardness to decrease. Moreover, extremely high dislocation density resulted from strain hardening of bulk-shaped material contributes directly in microhardness value. These arguments explain differences in microhardness of quasicrystalline materials performed by different processing routes.

Of importance is the aspect that concerns ductility of different kinds of quasicrystalline materials.

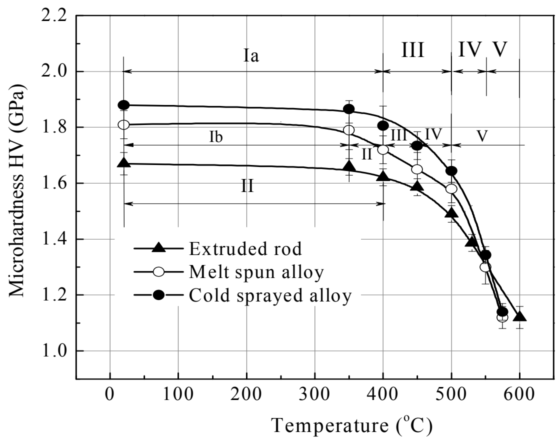

Fig. 4. The data for microhardness, HV, plotted against heat treatment temperature. Structural regions: Ia - α-Al+i-phase, Ib - α-Al+i-phase +nano-sized precipitates θ-$Al_{13}(Fe,Cr)_{2\text{-}4}$ /Al_6Fe, II - α-Al+i-phase+Al_6Fe, III - α-Al+ Al_6Fe, IV - α-Al + Al_6Fe +θ-phases, V - α-Al+θ - phases

The values of plasticity characteristic δ_H for different kinds of as-received quasicrystalline materials are listed in Table II. It is commonly supposed that material ductility increases as microhardness decreases. Actually, plasticity characteristic δ_H for the melt-spun alloy get higher values compared to cold-sprayed alloy whose microhardness, HV, is higher. From the above viewpoint it is surprising for the first glance that, plasticity characteristic δ_H of extruded material takes the smallest values despite of the most reduced microhardness, HV. Explanation of this phenomenon concerns the fact that plasticity characteristic δ_H is also controlled by Young's modulus besides microhardness [14]. Moreover, plasticity characteristic δ_H tends to decrease as a ratio of microhardness, HV, to Young's modulus, E, increases, see data in Table II. Indeed, plasticity characteristic δ_H increases with increasing heat treatment temperature since the values of microhardness, HV, and Young's modulus, E, are also reduced. Thus, the smallest values of plasticity characteristic δ_H, which were determined for the extruded material over the all range of annealing temperatures, become understanding by accounting the smallest values of Young's modulus caused by the reduced fraction volume of quasicrystalline particles.

It is essential that plasticity characteristic δ_H of quasicrystalline Al-Fe-Cr alloy fabricated by different techniques is just below critical value, $\delta_H = 0.9$, which is presently considered as criterion of ductile behavior of metals and alloys in conventional tests by tensile and bending [14]. Thus, all of the processing routes are thought to be potentially suitable for performance of quasicrystalline structure for Al-Fe-Cr alloy which demonstrates high strength combined with sufficient ductility. However, as applied to structural performance of bulk-shaped composites based on ternary Al-Fe-Cr alloy, cold-spraying offers essential advantages compared to hot extrusion currently employed in engineering practice.

IV. Conclusions

Essential differences in microstructure, heat treatment response, and mechanical properties of nanoquasicrystalline composite based on $Al_{94}Fe_3Cr_3$ alloy and performed by different processing routes including melt spinning, water atomization, hot extrusion, and cold spraying were found and specified.

As applied to semi-products, grain boundary precipitates and fine particles of metastable crystalline $Al_{13}(Fe,Cr)_{2\text{-}4}/Al_6Fe$ phases inside the α-Al grains of as-spun alloy were found besides nano-sized quasicrystals of icosahedral phase (i-phase) indicative of atomized powder. In addition, dislocation density recorded in α-Al matrix of as-atomized powder was believed to be higher by 2 order magnitude compared to that of as-spun alloy, i.e. $\rho = 10^{11}$ m/m^3.

Additional alterations in microstructure of composite based on Al-Fe-Cr alloy are resulted from processing route used for consolidation of atomized powder in bulk-shaped material. Powder pre-compacting at the temperature of 350 °C followed by hot extrusion favors partial dissolution of quasicrystalline particles together with creation of more stable crystalline particles of Al_6Fe-phase while dislocation density of α-Al solid solution rise up to the value of 10^{16} m/m^3. As opposed to this, cold-spraying offers essential advantages in remaining quasicrystalline particles presented in feedstock powder since adiabatic increase of temperature affects only particle/particle interface although dislocation density in α-Al matrix increases up to 10^{15} m/m^3.

Structural evolution of quasicrystalline Al-Fe-Cr alloy under heat treatment was strongly dependent on microstructure of as-received material. In particular, the presence of ultrafine crystalline precipitates in microstructure of the as-spun alloy promotes formation of big in size crystalline particles of metastable Al_6Fe phase, shifting their formation toward smaller by 50 °C temperatures as compared to atomized powder. High dislocation density in heavily deformed structure of bulk-shape materials facilitates decomposition of quasicrystalline particles and simultaneous formation of crystalline phases, resulting in shift of phase transformation peak by 50 °C toward smaller temperatures as compared to feedstock atomized powder.

Generally, all kinds of composite materials based on Al-Fe-Cr alloy show superior combination of high strength and sufficient ductility. However, cold-spray technique provides the highest values of both microhardness and plasticity characteristic δ_H for composites based on Al-Fe-Cr alloy, making them competitive to commercial Al alloys recommended for application under intermediate temperatures.

TABLE II. Mechanical Characteristics of As-Received Composite Materials

Material	**Characteristic**		
	Plasticity characteristic δ_H	***Young's modulus E (GPa)***	***HV/E***
Melt-spun alloy	0.84	85.0±2.2	2.13×10^{-2}
Extruded material	0.82	72.0± 2.3	2.31×10^{-2}
Cold-sprayed alloy	0.84	87.7±2.5	2.14×10^{-2}

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